Photopyroelectric Determination of the Order of Liquid Crystal Phase Transitions¹

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ABSTRACT

The photopyroelectric technique has been used to simultaneously measure the

specific heat, the thermal conductivity and the thermal diffusivity of 9CB liquid crystal in

the temperature range 35-60 °C where the sample undergoes a weakly first order phase

transition and a second order one. Measurements of the anisotropy of the thermal

conductivity (k) have been also performed and the data have been used to establish the

order of the above mentioned phase transitions. Pretransitional effects in the isotropic

phase in the thermal diffusivity have been found and they have been associated to similar

effects reported for the specific heat.

KEY WORDS: liquid crystals, phase transitions, thermal conductivity

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INTRODUCTION

It is possible to establish whether a phase transition has a first order character just detecting the latent heat associated with the transition itself. a.c. calorimetric techniques, however, which are based on the detection of temperature oscillation in the sample generated by a periodic heating, cannot detect the latent heat and it is generally believed that they are not suitable to discriminate between a first and a second order phase transition. In this paper we will show that if an a.c. calorimetric technique is sensitive to the anisotropy in thermal parameters, it can be used to perform high resolution measurements devoted to the determination of the order of a phase transition. The photopyroelectric technique [1] has been used to simultaneously measure the specific heat (c), the thermal conductivity (k) and the thermal diffusivity (D) of 9CB liquid crystal in a temperature range 35 - 60 °C, where it undergoes the Smectic A - Nematic (AN) and the weakly first order Nematic - Isotropic (NI) phase transition. Though there are many data in literature, especially specific heat data, showing that the AN transition is a second order one [2], some doubts still remain [3]. Measurements of the anisotropy in k and D have been performed and they have been associated to the order parameter. A discontinuity in this quantity at the transition temperature is a signature of a first order phase transition, while a continuos order parameter means a second order transition. We have found a clear discontinuity at the NI transition while high resolution measurements at the AN one do not show any discontinuity. Some features observed in the order parameter close to the AN transition will be discussed and finally pretransitional effects in the isotropic phase close to the NI transition will be reported.

MEASUREMENTS

A standard photopyroelectric setup [1] has been used for the measurements. The sample was contained in 30 µm cell and the temperature oscillation introduced by a periodic heating was detected by a LiTaO₃ pyroelectric transducer which was the cover of one of the cell sides. Heating on the opposite side was produced via the absorption of a He-Ne laser light modulated at 26 Hz by a very thin (~ 200 nm) optically opaque and thermally transparent Ti layer in contact with the sample.

The liquid crystal molecules can be roughly described as rigid rods and it has been shown that the thermal conductivity is larger along the long molecular axis than the one along the short axis $(k_{\parallel} \triangleright k_{\perp})$ [4,5,6]. The anisotropy in the thermal conductivity and therefore in the thermal diffusivity can be investigated aligning the molecules in given directions. In our case the molecules have been aligned with the long axis parallel (homeotropic alignment) and perpendicular (planar alignment) to the hear flow direction. In the first case we have measured k_{\parallel} , while in the second case k_{\perp} was obtained. The homeotropic alignment has been achieved treating the cell walls with a trimethylcethylammonium bromide solution, while the planar one has been obtained sputtering a thin layer of quartz at an angle of about 60°. The alignment has been checked using a polarizing microscope. Two different heating rates have been used for the measurement on a wide temperature range and the high resolution ones performed close to the transition temperature: in the first case the heating rate was 0.5 mK/min, while in the second case it was 20 mK/min.

RESULTS

Fig. 1 shows the specific heat in the temperature range 35-60 °C for the homeotropic and planar samples. As expected, the two curves superimpose quite well,

showing no remarkable differences in the two cases. The two peaks correspond to the AN transition at 47.8 °C and to the NI transition at 49.7 °C.

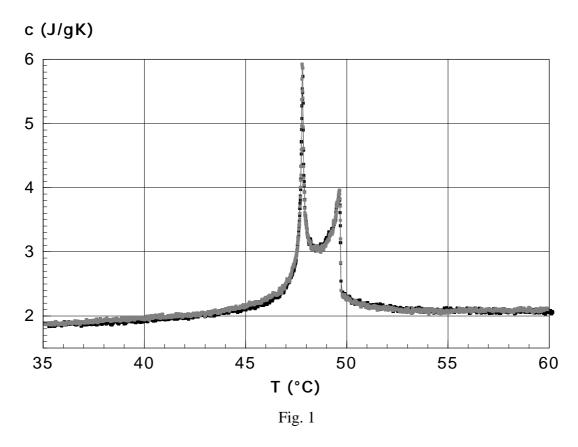
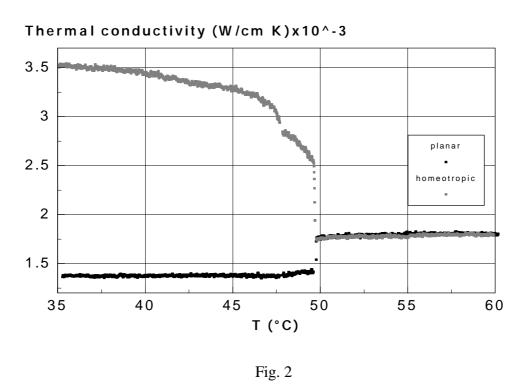


Fig. 2 reports the k data for the two different alignments. The same values for k_{\parallel} and k_{\perp} have been obtained in the isotropic phase, while in the Smectic and Nematic mesophases, $k_{\parallel} \!\!>\! k_{\perp}$. A jump in both the cases is clearly visible at the NI transition and while k_{\parallel} increases with decreasing temperature, k_{\perp} slightly decreases in the Nematic phase and then remains approximately constant in the Smectic phase. Similar results have been recently obtained for 5CB [5] and 8CB [6]. In all cases there is a much slower temperature dependence of k_{\perp} with respect to k_{\parallel} . Such a behavior can be understood if one consider the temperature dependence of the orientational order parameter which accounts for the average orientation of the molecules along a given direction. This parameter increases with decreasing temperature and therefore an increase of k_{\parallel} and a

decrease of k_{\perp} should be expected. The different temperature dependence of the conductivity could be due to the different slopes of the k vs. θ curve close to $\theta=0$ and $\theta=\pi/2$, where θ is the angle between the molecule long axis and the direction of the heat flow. Assuming rod-like molecules and, after Rondelez et al. [4], tempting the analogy between liquid crystal molecules and crystalline grains in a polycrystalline material, the thermal conductivity in a given direction is dominated by the number and the size of (grain) boundaries. This simple analogy can account for the larger k in the homeotropic case with respect the planar one, since for a fixed thickness and due to the elongated shape of the molecules, the number of boundaries encountered along the heat flow direction in the homeotropic case is lower than the ones encountered in the planar case.



Another interesting feature which can be detected in Fig. 2 is the clear change in the temperature dependence of k_{\parallel} close the AN transition temperature: a steeper increase of k_{\parallel} with decreasing temperature on the Smectic side with respect to the Nematic one is

evident. On the other hand minor changes appear in k_{\perp} in the same temperature range. One possible hypothesis to explain such a behavior is related to the structure of the Nematic and Smectic A phases. In the first case the molecules are preferentially oriented along a given direction, which in the case of a homeotropic alignment for example, is parallel to the heat flow direction. There is no correlation among the centers of mass of the molecules. The Smectic A phase, on the other hand, can be regarded as a stack of planes in which all the molecules are preferentially oriented with the long axis perpendicular to the plane with no in plane correlation. A density modulation in the direction perpendicular to plane appears below the AN transition temperature and major changes in the heat transport properties could be therefore expected only for heat propagation along this direction. Measurements in a liquid crystal having a Smectic C phase [4], in which the molecular long axis is tilted with respect to the normal to the planes z, however, show no particular features along z, while a maximum in the conductivity has been found again along the long molecular axis. A more plausible explanation could be related to an increase in the orientational order in the Smectic phase with respect to the Nematic one due to the appearance of smectic layers. The effect shown in Fig. 3 is more evident in the present case than the one reported for 8CB [6]. This could be due to the width of the nematic range of 8CB that is much larger (about 7K) than the one of 9CB. Since the orientational order increases with decreasing temperature in the Nematic phase, it can approach more closely the Smectic one in 8CB than in 9CB where the AN transition is only a couple of degrees away from the NI one.

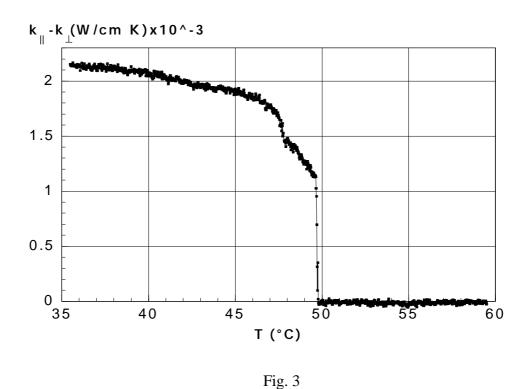


Fig. 4 shows the temperature dependence of the thermal diffusivity D and of the thermal conductivity k in the isotropic phase. It is clearly evident that D starts to decrease much far away than k. Such a decrease can be related to pretransitional effects due to presence in the isotropic phase of pseudonematic and pseudosmectic domains which appear and disappear temporally and spatially [7]. The relaxation time of such a domains increases when T_{AN} is approached [7] but this phenomenon affects the thermal diffusivity only and not the thermal conductivity. Now, since $D = k / (\rho c)$, where ρ is the density, the observed pretransitonal effect in D must be correlated with a similar pretransitional effect in c, being ρ approximately constant in the temperature range of Fig. 4 [8].

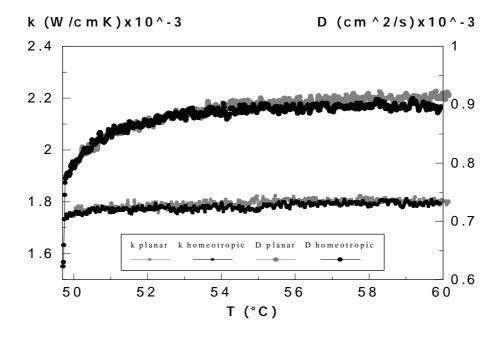


Fig. 4

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